Historic, archived docume

Do not assume content reflects curre
scientific knowledge, policies, or prac

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS—BULLETIN NO. 25.
MILTON WHITNEY, Chief.

CONTRIBUTIONS TO OUR KNOWLEDGE OF THE AERATION OF SOILS.

BY

EDGAR BUCKINGHAM.

1862 1889

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1904.

LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., November 8, 1904.

Sir: I respectfully transmit herewith a technical report, entitled "Contributions to our Knowledge of the Aeration of Soils," by Dr. Edgar Buckingham, of the Physical Laboratory of this Bureau, and recommend that it be published as Bulletin No. 25 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

LETTER OF SUBMITTAL.

U. S. Department of Agriculture,
Bureau of Soils, Physical Laboratory,
Washington, D. C., November 8, 1904.

Sir: I respectfully submit herewith the manuscript of a technical bulletin, entitled "Contributions to our Knowledge of the Aeration of Soils," prepared by Dr. Edgar Buckingham, of this Laboratory.

This paper presents for the first time definite information regarding the rate at which a gas escapes by diffusion from the soil into the atmosphere, or vice versa. It is shown that the rate of diffusion varies approximately as the square of the porosity of the soil, and that this diffusion follows the laws for the free diffusion of gases. It thus becomes possible to calculate the rate of aeration in any particular soil from results obtained in experiments on free diffusion. Tables are given showing the rate of escape (and consequently, for a condition of equilibrium, the rate of formation as well) of carbon dioxide in the soil when the porosity of the soil and the concentration of the carbon dioxide at any given depth are known. The paper shows further that the aeration of soils is almost entirely due to diffusion phenomena, changes in barometric pressure having very little influence in comparison.

Respectfully,

Lyman J. Briggs,
Physicist in Charge.

Prof. Milton Whitney,
Chief of Bureau.

CONTENTS.

Page.

Introduction 7

Preliminary experiments 8

  Transpiration 8

  Diffusion 8

Method finally adopted—apparatus 9

  The soil case 9

  The pressure-gauge 10

  The aspirator 10

  The gas-pressure regulators 11

  The collecting apparatus 12

Method of operation 13

Definition and mode of determination of porosity, transpiration constant, and diffusion constant 14

  The porosity 14

  The transpiration constant 15

  The diffusion constant 16

Transpiration of carbonic acid 17

Summary of results on transpiration and diffusion 18

Empirical conclusions from the experimental data 22

  Relation between porosity and speed of diffusion 22

  Relation between diffusion through soils and free diffusion 23

  Relation between porosity and speed of transpiration 25

The penetration of barometric waves into the soil 26

  Variations of pressure actually to be expected 31

  Actual amounts of rinsing possible 32

The movement of gases through soils by pure diffusion 33

  The free diffusion of two gases 33

  The diffusion of two gases through a third gas 34

  The distribution of nitrogen in the soil 34

  The rates of diffusion of carbonic acid and oxygen through nitrogen 37

The effect of barometric changes on the escape of carbonic acid by diffusion 41

The diffusion of other gases through the soil 45

Concluding remarks 45

Appendix A: The penetration of barometric waves into the soil 47

Appendix B: The diffusion of two gases through a third 51

CONTRIBUTIONS TO OUR KNOWLEDGE OF THE AERATION OF SOILS.

INTRODUCTION.

The object of this paper is to add to our information regarding the aeration of soils, primarily the escape of carbonic acid gas from its seat of formation in the soil, and the entrance of oxygen to take its place. The specific points treated are: (1) The relative importance of diffusion and of changes in barometric pressure; (2) the influence of texture, structure,[a] and compactness; (3) the actual amounts of carbonic acid leaving and of oxygen entering the soil under definite conditions of temperature, porosity, and composition of the soil atmosphere.

The experimental work deals (1) with the mixing of carbonic acid and air by diffusion through layers of soil of known area, thickness, and porosity when the total pressure is kept the same on both sides of the soil layer, and (2) with the rate of flow of air through the same layer of soil in precisely the same physical state under the influence of a slight excess of pressure on one side of the layer. This flow of air under pressure is similar to the flow or "transpiration" of air through capillary tubes. It will therefore, for brevity, be referred to as transpiration.

The soils used were of several types, each in various states of compactness, etc., and while the experimental results are few, because of the great time expended in searching for suitable methods of experiment and by the actual measurements even after fairly satisfactory methods had been devised, it is believed that the results are sufficient to warrant some general conclusions.

The theoretical deductions from the experimental results have been kept as far as possible in non-mathematical form. Some of the mathematical work which was necessary in arriving at the conclusions will be found outlined in two appendices.

---

[a] The term "structure" is, for brevity, used with the meaning "state of granulation."

PRELIMINARY EXPERIMENTS.

TRANSPIRATION.

The first experimental work done was on transpiration. The method used was to observe the rate of fall of the pressure of the dry air in a 14-liter bottle, as the air escaped through a column of soil of some 20 cm. to 60 cm. in length, contained in a glass tube of from 3 cm. to 4 cm. inside diameter. The soil tube was placed vertically, with the soil resting on a piece of fine brass wire gauze supported from below. The pressures were read on a sulphuric acid gauge.

The results of these experiments showed (1) that the rate of transpiration was very nearly proportional to the fall of pressure per centimeter of soil, i. e., to the pressure gradient; and (2) that the rate of transpiration through a given soil was very greatly dependent upon the structure and the manner of packing.

Great difficulty was experienced from adiabatic heating and cooling, and the method was abandoned in favor of a much simpler one like that used by King[a] in which air was drawn through the soil by a small tank aspirator, while the excess of pressure was measured by a small inclined water gauge.

DIFFUSION.

As in the case of transpiration, the methods first tried were much less simple in theory than that finally adopted. In the first experiments a plug of soil was supported on wire gauze in a wide glass tube. Below the soil was a layer of coarse sand wet with an alkaline solution of pyrogallol. The upper end of the tube was connected with a gas burette for measuring changes of volume at constant pressure, while the lower end was closed air-tight. Time readings were made of the decrease of volume of the air inclosed in the tube and burette as the oxygen passed through the soil plug and was absorbed by the pyrogallol. The observations, while simple and regular enough when plotted graphically, did not admit of any simple reduction leading to the desired information, and only a few experiments of this sort were made.

An attempt was also made to use Bunsen's method for the diffusion of gases through a porous plug. A wide glass tube was stopped at the top by a plug of the soil to be studied. The bottom of the tube was provided with a water pressure-gauge and with tubes by which the large glass tube could be filled with carbonic acid. In such an experiment as this, if the plug separating the inclosed carbonic acid from the outside air be sufficiently fine grained, the air entering the tube faster than the carbonic acid escapes causes a rise of pressure.

---

[a] Nineteenth Annual Report, U. S. Geological Survey, Part II, 1899.

In the present case, however, the ease of transpiration through the plug of soil was so great that no measurable increase of pressure was observed inside the tube, so that the method was useless.

These two methods having been found impracticable, an attempt was made to run streams of carbonic acid and air across the ends of a plug of soil, keeping the pressure on the two ends precisely the same so as to eliminate transpiration. Analyses of the gases before and after passing by the soil, together with measurements of the rates of flow, were expected to show how fast the gases had mixed by pure diffusion through the given layer of soil. After many trials and modifications of the apparatus, this method was, in principle, the one finally adopted as the least unsatisfactory yet found, and by it were obtained the results on diffusion to be given later.

METHOD FINALLY ADOPTED—APPARATUS.

It had been shown by the preliminary experiments on transpiration that even a slight jarring might cause a very large change in the speed of transpiration of air through a soil. Hence, as it was hoped to find some relations between transpiration, diffusion, and porosity, it was necessary to be able to make both the transpiration and the diffusion experiments without disturbing the soil in the least. This end was attained by the use of the following apparatus:

THE SOIL CASE.

The soil was inclosed in a rectangular brass box or soil case 8 inches long, 2½ inches wide, and 4 inches high inside. The top and bottom of the box were flanged, and could be closed gas-tight by covers screwed down on rubber packing. In the bottom of the box was a gridiron frame about 2 cm. high of thin sheet brass set on edge, and resting on this was a piece of galvanized-iron wire net of ⅛-inch mesh. Over the net was a piece of cheese cloth, and on the cloth rested the soil. The gridiron frame fitted loosely into the box, and was cut out so as to allow free communication throughout the space between the bottom of the soil case and the bottom of the soil. Close to each of the eight corners of the box was soldered on a short piece of brass tube of ¼-inch internal diameter, by means of which connections could be made with the rest of the apparatus. When all these tubes were closed the soil was shut up air-tight and could be left standing without fear of its gaining or losing moisture. By removing the top cover the soil could be compressed or wet without disturbing any of the connections. When a new soil was to be used, the rubber tubes leading to the other parts of the apparatus were disconnected from the soil case, and the case opened and cleaned before the new soil was introduced.

THE PRESSURE-GAUGE.

For both transpiration and diffusion experiments it was necessary to have a gauge connected with the soil case above and below the soil. The gauge consisted of a bent glass tube of about 4 mm. inside diameter, with its parallel arms about 8 mm. apart from center to center. This tube was clamped on a brass frame provided with leveling screws so that its position could be adjusted. The slope of the gauge was always about 1 in 10. Under the tube was a paper scale divided to twentieths of an inch. The scale was no wider than necessary, and was shellacked on a strip of mirror about an inch wide which helped the observer to avoid parallax errors in reading. The mirror and scale lay between the brass frame and the tube. The tube was partly filled with water. If it was clean, and if care was taken always to have the tube wet above the meniscus in both arms, it was very sensitive to differences of pressure between the two arms. With a slope of 1 in 10, a difference of one scale division between the two arms meant a difference in pressure of 0.0093 mm. of mercury. Readings could easily be made to less than half this amount. Before using the gauge in any experiment it was always adjusted by the leveling screws so that the meniscus in each arm gave the same reading. One arm of this gauge was connected to the soil case below the soil, and the other above it, and by its aid the difference of pressure above and below the soil could be determined. Each arm of the gauge was so connected that it could be shut off from the soil case and opened to the outside air for adjusting the zero.

THE ASPIRATOR.

For the measurements on transpiration an aspirator was used. This consisted of a sheet-copper can about 8 inches in diameter and 9 inches high, inverted over water in another copper can 9½ inches in diameter. The suction tube and an extra discharge tube came up through the bottom of the outer or fixed can. The inner can had a brass stem 16 inches long rising from the middle of the top, and running loosely through a brass guide. The whole was suspended by a fine brass wire attached to the top of the stem and running over an 8-inch grooved wooden pulley to a weight. The weight could be varied by adding or taking off smaller lead weights, and so the suction of the aspirator varied within the desired limits. The volume of the can was found by calibrating with water. A vertical scale divided into twentieths of an inch was attached to the top of the movable can by a horizontal arm, so that it played up and down past an index outside the fixed can as the aspirator drew in or drove out air. The volumes of air drawn in could thus be found from the rise of the can as shown by the changes in position of the scale with regard to the fixed index.

The aspirator was so connected to the soil case that by changing a couple of pinchcocks it could be made to suck gas from either above or below the soil, or be cut off altogether.

THE GAS-PRESSURE REGULATORS.

For the diffusion experiments it was necessary to have, passing by the top and bottom of the soil, a stream of air and a stream of carbonic acid under as nearly equal pressures as possible. The air was supplied by a Chapman pump drawing air from outside the window and blowing it into a bottle, whence it passed to the rest of the apparatus. The carbonic acid was drawn from a cylinder of commercial gas as supplied for soda fountains and other similar purposes. From the valve on this cylinder, which lay horizontally, the gas passed immediately to a regulator made of a bicycle pump. This was so arranged as to be capable of moving a bar fixed to the stem of the valve on the storage cylinder. If the pressure in the regulator cylinder rose too high its piston was driven up and the valve screwed shut. When the pressure fell off again, weights hung on the piston rod opened the valve. After passing through this regulator the gas bubbled through water, passed through a safety-valve arrangement, made of a 2-liter bottle, which permitted the gas to blow off out the window when the pressure rose above a certain head of water, and so on to the rest of the apparatus.

So far the two streams of gas were by no means of constant or equal pressure—the air because of changes in the water pressure operating the pump, and the carbonic acid because of the imperfect action of the regulator just described. The inequalities of the pressures of the two gases were next reduced by passing them through a duplex gasometer pressure regulator. Two copper cans, 4½ inches in diameter and 3½ inches deep, were attached, bottom up, with their centers 14 inches apart, to a wooden beam balanced in the middle on a steel knife-edge. The cans could thus oscillate up and down over water in two other cans below them. The stream of air was led, by tubes coming up through the bottom of one of the fixed cans, through the movable can over it, while the carbonic acid was led through the other can in the same way. Each gas came to its can through a piece of $\frac{3}{16}$-inch thin-walled black rubber tubing. These thin rubber tubes were compressed between fixed brass surfaces and brass edges fixed to the beam. If the air pressure, for example, became too great, the air can rose and the rubber tube bringing the air was compressed, while that bringing the carbonic acid was allowed to open by an equivalent amount.

When the gases were running through this regulator the beam was in a state of constant oscillation through a very small range; and though it was not, in principle, capable of giving perfect regulation, because of the elasticity of the rubber tubes, it usually kept the pressures of the emerging streams of gas equal within somewhat less than half a millimeter of mercury.

From this automatic regulator the gases were led through rubber tubes to the soil case, but on the way they passed through a third and final regulator. This was a sort of pinchcock with a lever compressor worked by a large milled head. By turning this head in one direction the air tube was closed while the carbonic-acid tube was opened, and vice versa. During an experiment on diffusion the observer kept one hand on this pinchcock, and, with his eye on the gauge, could easily keep the readings in the two arms of the gauge within one scale division, or less than 0.01 mm. of mercury. The average difference of pressure indicated by the gauge was probably in general not over 0.002 mm. of mercury in any one experiment, and was as likely to be in one direction as in the other.

THE COLLECTING APPARATUS.

The two gases having thus arrived at the soil case, passed, the one diagonally over the top of the layer of soil and the other diagonally under the bottom, along different diagonals. After issuing from the soil case they bubbled out under water through glass tubes of about 3 mm. bore, at a depth of three-fourths inch below the surface of the water, and were collected when desired in two inverted half-liter bottles. The water was, of course, in separate tanks, and the collecting bottles were so mounted on a slide that by a single motion of the hand both of them could be slid over the discharge tubes or withdrawn.

After collection the gases were transferred to a Hempel gas burette, and the percentage of carbonic acid determined by absorption in caustic potash. The burette was jacketed with flowing tap water and the analyses were corrected for pressure and temperature.

Beside the paths for the gases through the soil case, there were two by-passes by which the gases could be led to the collection tanks through all the apparatus except the soil case. In this way the composition of the two streams of gas, at least as regards carbonic acid, could be determined before they entered the soil case. It was found that the amount of carbonic acid in the air was negligible, and in the later work no more tests were made on it. The composition of the carbonic acid from the storage cylinder was found to vary considerably. The amount of gas absorbable by a concentrated KOH solution varied from 97.3 per cent to 98.5 per cent in the case of the first cylinder used and from 95 per cent to 97.5 per cent with a second cylinder. If the cylinder was undisturbed, the change in the analyses indicated a slight regular decrease in the amount of impurity coming from the cylinder with the carbonic acid, hence it was found necessary to make analyses only occasionally.

METHOD OF OPERATION.

In starting a set of experiments on a given soil the soil case was disconnected from the rest of the apparatus, opened, emptied, and cleaned. The wire grating and cheese cloth were placed on the gridiron, and the case was then ready for the soil. This was first broken up fine in a mill. If it was to be used air-dry, it was then, after thorough mixing, put directly into the soil case. If the soil was to be used moist it was worked up by hand with the desired amount of water and mixed very thoroughly. The soil case was then filled to within a half an inch of the top, and the cover laid on. Meanwhile a sample of 100 to 200 grams had been weighed out for the moisture determination. This sample was later, whenever convenient, dried at 110° C. for at least six hours and weighed again to complete the moisture determination. Before screwing down the top of the soil case the soil was smoothed off and pressed down lightly with a wooden block which fitted loosely into the case. The depth to the surface of the soil was found by drawing a line around this block with a sharp pencil. The mean distance of this line from the lower face of the block subtracted from the mean distance from the upper edge of the case to the cheese cloth gave the mean thickness of the soil. The line having been drawn on the block, the soil case was closed, weighed, and connected to the rest of the apparatus.

The first experiment was always one on transpiration. Four or five liters of outside air were, by opening and closing the proper pinchcocks, drawn through the soil into the aspirator, and the elapsed time noted. The gauge readings and the temperature of the room were noted meanwhile at frequent intervals. If the transpiration was very rapid a stop watch was used, but generally an ordinary watch with seconds hand was amply sufficient. The difference of pressure used varied from 9 mm. of mercury to 0.5 mm., and was seldom over 5 mm. These differences of pressure were small enough that no disturbances from adiabatic cooling were to be feared. Numerous tests showed that the rate of transpiration was sensibly proportional to the difference of pressure; hence it was not necessary always to use any one particular difference, and the weights on the aspirator were adjusted in each case so as to give a convenient rate of rise.

After at least two such experiments the aspirator was cut off, and the streams of air and carbonic acid were sent through the soil case. The collecting bottles were then filled with water from their respective tanks, and set up ready to be slid over the discharge tubes. The gases were thus sent through the apparatus for from ten to thirty minutes to insure thorough rinsing. During the first part of the time the pressures were left to the automatic duplex regulator, but during the last few minutes the observer kept the pressure adjusted as closely as possible by hand. When the collection was to begin the bottles were slid over the discharge tubes and the stop watch started. When the bottles were full the watch was stopped; meanwhile the pressures had been continually adjusted to as near equality as possible. The bottles seldom filled in just the same time, so that an allowance had to be made for the one which filled first, by reading the watch before stopping it. The resistances to flow were adjusted from time to time by screw pinchcocks between the soil case and the discharge tubes, so as to keep the rates of discharge under equal pressures as nearly equal as possible, and so avoid large errors in the estimation of the time. The time taken to fill the bottles was from twenty seconds to two minutes. After the bottles were full of gas they were slid away from the discharge tubes, closed by rubber stoppers, and left with their mouths under water in the tanks. The streams of gas were then cut off, and all openings into the soil case closed gas-tight.

For analysis the gas was displaced, by water from its own tank, into the gas burette. The water in the burette was also taken from the tank over which the gas had been collected. The gas from the carbonic acid side was usually analyzed first. The measurement of volume, absorption by caustic potash, etc., were carried out in the usual manner.

After such an experiment, the experiment on transpiration was repeated, then again diffusion, etc. In a few cases only one diffusion run was made, but generally there were at least two; and if the results of the first two did not agree fairly well, from one to three more were made. In any case transpiration was always alternated with diffusion, the set ending with transpiration.

After a set of experiments had been made in this way the top of the soil case was taken off and the soil compressed, tamped, or watered, as the case might be, after which the new depth to the soil was measured as before, the cover put on, and a new set of experiments begun.

DEFINITION AND MODE OF DETERMINATION OF POROSITY, TRANSPIRATION CONSTANT, AND DIFFUSION CONSTANT.

THE POROSITY.

By the porosity of the soil we mean that fraction of its total apparent volume which is unoccupied by either water or solid soil grains, and which is therefore filled with gas. This quantity will be denoted by S. For example:

Let the total apparent volume of the soil be 550 cm^3.
Let the total weight of the moist soil be 770 grams.
Let its moisture content be 10 per cent of the dry weight.
Let the true density of the soil grains be 2.67.

Then:

The weight of the dry soil is 770÷1.10 or 700 grams.

The true volume of the dry soil is 700÷2.67 or 262 cm^3.

The volume of the water is 70 cm^3, so that the total volume of soil grains and water is 262+70 or 332 cm^3. The free pore space is therefore 550−332 or 218 cm^3, and the porosity is 218÷550 or 0.396, i. e., we have $S=0.396$.

The determination of the porosity depends upon a knowledge of the apparent volume of the soil, its moisture content, and the true density of the soil grains. It also depends, as we have computed it, upon the assumption that the water in the soil actually occupies the same volume as an equal mass of water would occupy, if in mass instead of spread out in thin films over the soil grains, as a considerable part of it is if the soil is only moderately moist.

This assumption is somewhat doubtful. It seems probable that water thus spread out in thin films may have a specific volume very sensibly different from 1. A considerable error may always occur in the gravimetric determination of the moisture content of a soil. Furthermore, during the course of a set of experiments, the moisture content of the soil may vary considerably, the soil drying out during the transpiration runs, or gaining moisture by contact with the wet gases during the diffusion runs, if it happens to be colder than the inflowing gases. For all these reasons the allowance to be made for the volume of water in the soil is uncertain, and it was therefore not thought necessary to attempt to measure the thickness of the soil layer closer than to about one-half millimeter, nor to make accurate determinations of the true density of the soil grains. Hence the values to be given for the porosity, S, may be in error by several per cent. These sources of error might have been partially avoided or allowed for by sufficient care, but the expenditure of time which this would have necessitated did not appear warranted by the objects in view, and the possibilities of error in the other parts of the work.

THE TRANSPIRATION CONSTANT.

The results of the experiments on transpiration are expressed by means of the transpiration constant. By this we mean the number of cubic centimeters of air which would, in one second, flow through 1 cm^2 of cross section of a layer of soil 1 cm. thick, if the pressure were 1 mm. of mercury greater on one side of the layer than on the other. This transpiration constant will be denoted by T. For example:

Suppose that 3.6 liters of air are drawn by the aspirator through a layer of soil 100 cm^2 in area and 5 cm. thick, in two minutes, by a suction of 2 mm. of mercury. The total flow per second is 3600÷120, or 30 cm^3 per second. The flow through each square centimeter is 30÷100 or 0.3 cm^3 per second. The pressure gradient is 2 mm. in

5 cm. or 0.4 mm. per centimeter. Therefore the flow per second through each square centimeter for a gradient of 1 mm. per centimeter would be 0.3÷0.4 or 0.75 cm^3, or we have $T=0.75$.

According to the work of earlier experimenters, it appears that the velocity of transpiration is approximately proportional to the seven-tenths power of the reciprocal of the absolute temperature. The values of T were therefore reduced to 0° C. by the formula

$$T_0 = T \left\{ \frac{273+T}{273} \right\}^{0.7}$$

and the values tabulated later are not the values as measured, but these reduced values.

The determination of the transpiration constant depends upon a knowledge of the rate of flow, the difference of pressure, and the thickness and cross section of the soil. Of these quantities the thickness of the soil was probably, in general, the most uncertain, and the cross section the least so. The rate of flow, depending upon a volume which, even if erroneously measured, was always the same except in a very few cases, and upon a time which could easily be determined within much less than 1 per cent, was the most accurate of the variable quantities to be measured. The errors in the pressure, due to zero errors of the gauge, errors in measuring the slope, and sticking of the meniscus in the tube, were not large, as was shown by the consistency of the results. It is probably safe to estimate the errors of the values given for the transpiration constant as not over 1 or 2 per cent.

THE DIFFUSION CONSTANT.

The results of the experiments on diffusion are expressed by means of the diffusion constant. By this we mean the average number of cubic centimeters of each of two gases which would, in one second, pass in opposite directions through 1 cm^2 of cross section of a layer of soil 1 cm. thick, if the partial pressure of the first gas were 1 mm. of mercury greater on one side than on the other, and the partial pressure of the second gas, the same amount greater on the other side than on the one, the total pressure being the same on both sides. We say the average number of cubic centimeters because it appears that under the conditions of our experiments different gases do not diffuse through the soil with equal rapidity. This diffusion constant will be denoted by D. For example:

Suppose that with a layer of soil of 100 cm^2 cross section, and 5 cm. thickness, we find that in one second 0.057 cm^3 of carbonic acid pass through to the air side, while 0.083 cm^3 of air pass through to the carbonic acid side, the concentration of each gas having differed by 10 per cent on the two sides of the soil. The average flow has been $(0.057+0.083) \div 2$ or 0.070 cm^3 per second. The mean flow per square centimeter is 0.070 ÷ 100 or 0.0007 cm^3 per second. The difference of partial pressure is 10 per cent of 760 mm. or 76 mm., and the gradient is therefore 76 mm. in 5 cm. or 15.2 mm. per centimeter. Hence if the soil had been 1 cm. thick, and the difference of partial pressure had been 1 mm. of mercury, the flow would have been 0.0007 ÷ 15.2 or 0.0000461 cm^3 per centimeter per second. In other words, we have in this case, $D = 4.61 \times 10^{-5}$.

In the determination of the diffusion constant D there are numerous sources of error. There is the question of the thickness of the soil, though this, being constant for any one set of measurements of D, could not cause differences between values of D which should otherwise have been identical. The analyses of the gases are, of course, slightly inaccurate, and some error is introduced during the collection of the gases over water that was not precisely in equilibrium with them, but the possible errors due to these causes are much less than the actual differences found between values of the diffusion constant, which ought, judging from the conditions, to have been the same. The rates of flow, also, could not be determined with any very great accuracy. But these errors were probably all of minor importance. The main difficulty in the experiments was in keeping the pressures equal on the two sides of the layer of soil. This had finally to be regulated by hand and the regulation was imperfect, even supposing the gauge to work perfectly. For this reason the results of diffusion runs, which should have been determined by diffusion alone, were in fact always influenced to some extent by transpiration. The magnitude of the errors in the determination of the diffusion constant may be estimated from the summary of results which will be given. It is impossible to assign any exact limit.

TRANSPIRATION OF CARBONIC ACID.

Before going on to a general summary of the experimental results, it will be well to speak of the results of some experiments on the relative velocities of transpiration of air and carbonic acid, the carbonic acid being drawn from the cylinder of commercial gas and no corrections being made for its impurities. Several sets of experiments were made by running air and carbonic acid through the soil alternately and the transpiration velocities for the same pressure gradient measured. The results may be stated as follows:

Soil.	$\frac{\text{Vel. } CO_2}{\text{Vel. Air}}$
Moist garden loam : mean of 8 runs	1.184
Fine sand + 4.8 per cent H_2O : mean of 12 runs	1.242
Air-dry garden loam : mean of 6 runs	1.190

The weighted mean of these values is 1.21, or, the carbonic acid flowed 1.21 times as fast as air under identical conditions.

If the flow of gas through soils is really similar to the transpiration of gases through capillary tubes, this ratio of the speeds of flow should be the same as the reciprocal of the ratio of the viscosities of the gases in question. According to the work of former experimenters, the viscosity of air is larger than that of carbonic acid, the values given in Winkelmann's Handbuch der Physik (**1**, pp. 594, et seq.), showing a ratio of from 1.18 to 1.24. Our value of 1.21 lies between these limits, so that we are justified, from this point of view at least, in regarding the flow of gas through a soil under the influence of an excess of pressure as similar to that through capillary tubes, and in giving it the name of "transpiration."

In the course of these experiments tests were made to see whether the saturated air from the water pump gave different results from the outside air of the room, but no difference in behavior could be detected.

SUMMARY OF RESULTS ON TRANSPIRATION AND DIFFUSION.

The results of all the reliable experiments on diffusion and transpiration are summarized in Table I. A number of experiments in which only the transpiration was measured have been omitted from this table, as a consideration of them showed that including them would not modify to any sensible extent the conclusions to be drawn. A few other experiments of which there were a priori reasons to doubt the reliability have also been omitted.

The values of the porosity, *S*, are given in the second column. The values of the transpiration constant, *T*, given in the third column are averages of several runs. The separate values do not differ enough to make it worth while to give them in detail. The values of the diffusion constant, *D*, in the fourth column are the individual values obtained. The numbers given in the fifth column, headed *R*, show for each experiment on diffusion the ratio of the speed of diffusion of air to the speed of diffusion of carbonic acid as found from this particular experiment. These values will be used later.

TABLE I.

I.	II.	III.	IV.	V.
Soil.	S	T	$D\times10^5$	R
Dunesand, Eddy, N. Mex., 4.8 per cent H_2O	0.561	14.0	8.26	5.4
	0.460	2.15	4.82	2.09
			4.44	2.40
Garden loam, air dry	0.485	0.254	4.67	1.72
			4.80	1.68
	0.430	0.101	3.77	1.41
			3.55	1.44
Garden loam, 18.6 per cent H_2O	0.491	4.80	6.57	1.21
			5.09	1.57
			5.25	2.24
	0.399	1.437	3.92	1.26
			3.95	1.23
	0.319	0.451	2.59	1.67
			2.65	1.88
			2.68	1.57
Cecil clay, Statesville, N. C., 19.6 per cent H_2O	0.475	22.0	4.25	3.02
			4.63	7.60
	0.351	5.02	1.83	1.57
			1.88	0.81
			3.06	2.34
	0.249	1.245	1.75	1.40
			1.85	1.27
			1.85	1.15
Cecil clay, same as last, worked up with 20.1 per cent H_2O after air drying. Somewhat lumpy	0.463	22.6	3.76	2.10
			4.03	3.96
			5.09	3.03
			3.97	0.95
			3.84	1.88
	0.347	2.77	1.98	0.94
			1.91	1.65
S reduced by adding water, without compression	0.253	1.07	0.914	0.07
			0.594	4.58
			0.647	0.61
Cecil clay, same as last, air dry, coarse ground	0.609	22.0	5.16	1.53
			5.40	1.41
	0.520	5.08	3.36	1.40
			2.98	1.64
	0.468	0.114	2.83	1.21
			2.59	1.53
Windsor sand, subsoil, 4.2 per cent H_2O	0.549	21.3	7.53	1.76
			6.14	0.62
	0.331	1.898	3.14	1.95
			4.09	1.36
			3.29	1.45
S reduced by adding water, no compression	0.163	0.39	0.51	0.17

In Table II a more compact statement of the results is given, together with the results of certain computations which have been made upon them, to the end of discovering relations which may exist between porosity, transpiration, and diffusion.

TABLE II.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Kind and condition of soil.	Porosity, S.	Diffusion constant: Weighted means $D \times 10^5$.	Transpiration constant, T.		$\frac{D \times 10^4}{S^2}$	β	γ
Dunesand, 4.8 per cent H_2O........	0.561	8.26	14.0	2.83	2.62	3.33	9.44
	0.460	4.71	2.15	....	2.23	....	....
Garden loam, air dry..	0.485	4.73	0.254	....	2.01	....	....
	0.430	3.67	0.101	2.11	1.98	2.63	7.67
(H_2O added)........	0.312	2.56	....	1.39	2.63	....	....
Garden loam, 18.6 per cent H_2O........	0.491	5.29	4.80	1.61	2.19	3.42	5.51
	0.399	3.93	1.431	1.79	2.47	2.94	5.21
	0.319	2.64	0.445	....	2.59	....	....
Cecil clay, 19.6 per cent H_2O........	0.475	4.41	22.9	2.07	1.95	2.42	4.99
	0.351	2.36	5.07	....	1.92	....	....
	0.249	1.80	1.25	0.79	2.90	5.17	4.07
Cecil clay, 20.1 per cent H_2O........	0.463	3.89	21.9	....	1.81	....	....
	0.347	1.93	2.77	2.43	1.61	2.95	7.17
H_2O added........	0.253	0.61	0.937	3.07	0.95	[1.70]	....
Cecil clay, air dry.....	0.609	5.26	2.20	3.40	1.42	2.76	9.38
	0.520	3.08	0.508	....	0.83	....	....
	0.468	2.66	0.114	1.37	1.21	[10.32]	[14.17]
Windsor sand, subsoil, 4.2 per cent H_2O.....	0.549	7.50	21.3	1.64	2.49	2.92	4.77
	0.331	3.28	1.90	....	2.99	....	....
H_2O added........	0.163	0.51	0.387	2.63	1.91	[0.85]	....
Weighted means.......	....	....	....	1.94	2.16	....	....
Unweighted means....	....	....	....	2.09±0.14	2.04±0.09	....	....

Column I shows the kind of soil used and its condition.

Column II gives the porosity of the soil, *S*.

Column III gives the weighted mean values of the diffusion constant *D*, as obtained for this soil and with the porosity shown in Column II. The values are for convenience multiplied by 100,000.

In looking over the diffusion constants given in Table I, it will be seen that while values of *D*, which should be identical, are in fact sometimes quite near to each other, they sometimes show large divergences.

It was a question how to average these values, and some criterion had to be sought for assigning weights to the separate values of the diffusion constant in averaging. For this purpose the only thing available seemed to be the ratio R, tabulated in Table I. The assumption was, therefore, made that this ratio R has, in fact, a definite and constant value, and that the goodness or badness of a given experiment on diffusion may be estimated from the relation which its value of R bears to the most probable value of R. Since no criterion was available for weighting the values of R itself, the values in Column V of Table I, together with several others which were obtained from some preliminary experiments which did not permit any computation of the diffusion constant itself, were treated as of equal weight and averaged to give the most probable value of the ratio R. This value proved to be

$$R=1.85\pm 0.11$$

The probable error of the mean of 57 values was found by the usual process for observations of equal weight.

The following arbitrary method was then pursued in weighting the values of the diffusion constant D, which were to be averaged:

(1) We take the value of $(1.85\div R)$ for each experiment, i. e., we find the ratio of the most probable value of R to the actual value found in the experiment under consideration.

(2) We take the value of $[(1.85\div R)-1]$ without regard to sign, i. e., we see how far the quantity just found, namely $(1.85\div R)$, differs from its ideal value of $(1.85\div 1.85)$ or 1.

(3) We consider this difference $[(1.85\div R)-1]$ to be a measure of the unreliability of the experiment; and hence

(4) We assign to the value of D, obtained from this experiment, a weight proportional to the reciprocal of its unreliability, i. e., we give this value of the diffusion constant a weight:

$$\text{Weight}=\frac{1}{\left(\frac{1.85}{R}-1\right)}$$

By this somewhat complicated and altogether arbitrary method weights were assigned to all the values of D given in Table I. The values were then averaged by using these weights, and thus were obtained the weighted mean values of the diffusion constant given in Column III of Table II.

It will be noticed that this method of weighting would, in the case of an experiment which happened to yield the value $R=1.85$, give an infinite weight which would amount to the rejection of all other experiments from the averages—an absurd result. A different method of weighting, namely, that of using $\left[1-\frac{1.85-1}{6}\right]$ as the weight (where the difference, 1.85−1, was taken without regard to sign), was also tried later. The numerical conclusions to be drawn from the experiments are sensibly the same whether the observations be averaged directly, or whether they be first weighted by either of these two methods.

To return to Table II, Column IV gives the mean values of the transpiration constant T. The accidental errors in the determination of T were so small that there was no object in attempting to assign weights to the separate values before averaging. These three columns of figures, then, summarize the experimental data from which we have to draw our conclusions. The remaining columns of Table II contain the results of computations which were made in the course of studying the experimental data, and will be referred to in the next section.

EMPIRICAL CONCLUSIONS FROM THE EXPERIMENTAL DATA.

RELATION BETWEEN POROSITY AND SPEED OF DIFFUSION.

It was noticed, after only a few experiments had been performed, that when the porosity of a soil was reduced by compacting the soil by pressure from on top, or by taking it out of the soil case and tamping it back, the transpiration constant varied approximately as the cube of the diffusion constant. This led to the comparison of both of these quantities with the porosity, to see if any similar relations of the form

$$y = x^n$$

held there.

Let us first consider the variation of the diffusion constant with the porosity. What we shall do is to assume that there exists a relation of the form

$$D = \text{constant} \times S^{a}$$

and then determine the value of the exponent α. In the case of each soil—each filling of the soil case we should rather say—that pair of values of D and S was taken as the standard for which the value of D had the greatest weight, determined as described in the last section. These values obtained for the exponent α are given in column V of Table II opposite the values of D, from which they were obtained by combining with the standard value of D for that set. It will be seen that the values of α vary from 0.79 to 3.40, but that the mean values for the different soils do not differ more than the individual values for one soil differ among themselves. There seems to be no particular regularity in the figures, and nothing to disprove our assumption that the diffusion constant varies as a power of the porosity except a lack of closeness of agreement. These thirteen values of α were next averaged, giving each a weight proportional to the product of the weights of the two values of the diffusion constant used in computing it. They were also averaged without weighting. The results are:

Weighted mean value, $\alpha=1.94$.
Unweighted mean value, $\alpha=2.09 \pm 0.14$.

It appears, then, that the results for each soil may be represented approximately by the equation

$$D=\text{constant} \times S^2$$

and it remains to see whether the constant varies from soil to soil or is the same, and if it is the same, what its value is.

The value of the constant is evidently $(D \div S^2)$. The value of $(D \div S^2)$ was therefore computed for each of the 20 values of D given in column III of Table II, and the results are given in column VI. It appears from these figures that the constant does change somewhat from soil to soil, but not very much. We shall not be far wrong if we assume it to be the same for all the soils and take its mean value. The unweighted mean has been taken as well as the mean obtained by giving each value a weight proportional to the weight of the value of D, from which it was computed. The results are:

Weighted mean value, $10^4 \times \frac{D}{S^2}=2.16$.
Unweighted mean value, $=2.04 \pm 0.09$.

We thus arrive at the conclusion that our experimental results on the speed of diffusion of air and carbonic acid into each other through soils, as related to the porosity of the soils, may be represented approximately by the equation

$$10^4 \times D=2.16 \times S^2$$

which means that the speed of diffusion is proportional to the square of the percentage of free pore space, and that the texture, structure, and moisture content, while probably influencing the degree of approximation, do not do so to any very great extent.

RELATION BETWEEN DIFFUSION THROUGH SOILS AND FREE DIFFUSION.

The rather surprising conclusion just reached leads us to ask whether our results are not directly related to the speed of diffusion of air and carbonic acid into each other when no soil is present, and the diffusion is perfectly free. What we have done in finding the value of $(D \div S^2)$ is, in substance, to find the value the diffusion constant D would have, supposing our equation to be correct, if S were equal to 1, i. e., if the free pore space were 100 per cent of the whole apparent volume of the soil. But if the pore space were 100 per cent, we should have no soil grains present at all, and should have a case of perfectly free diffusion. Our results, then, lead us to suppose that if air and carbonic acid diffuse into each other freely, the number of cubic centimeters of each gas which in one second passes into the other through each square centimeter of cross section, if the partial pressure gradient is 1 mm. of mercury per centimeter, is

$$D_f = 2.16 \times 10^{-4}.$$

The question at once arises: How does this compare with the values already known from experiments on free diffusion?

The mean pressure at which our experiments were performed was 760.7 mm. or, nearly enough, 760 mm. The mean temperature of the room was 26.9° C. or, nearly enough, 27° C. Careful experiments on the free diffusion of air and carbonic acid have been made by Loschmidt[a] and Obermayer.[b] The mean of their results reduced to 27° C. and to a pressure gradient of 1 mm. of mercury per centimeter gives for the rate of free diffusion of air and carbonic acid

$$D_f = 2.20 \times 10^{-4}.$$

Their results differ by nearly 6 per cent, and would if computed separately give 2.26×10^{-4} and 2.13×10^{-4}, so that the value of D_f computed from our results, namely, 2.16×10^{-4} lies between them.

In view of the inaccuracies of our work it would be idle to pretend that so close an agreement is more than accidental. Nevertheless it is remarkable, and we may conclude from it that the diffusion of air and carbonic acid into each other through a soil is in fact merely a slightly modified case of free diffusion, and that, dangerous as the extrapolation to 100 per cent porosity by an exponential formula might appear, it has actually been justified by the results. Furthermore, since the experiments of Loschmidt and Obermayer were undoubtedly much more exact than ours, we may base ourselves on their work and say that we may, approximately at least, compute the rate of diffusion of air and carbonic acid into each other through the soils we have worked with, by multiplying the known rate for free diffusion by the square of the porosity of the soil, the rate for free diffusion being of course taken for the temperature and barometric pressure in question. This important and simple result will be referred to later when we are considering what actually happens in a soil where, instead of having air as a whole diffusing into carbonic acid, we have carbonic acid and oxygen diffusing into each other through a nearly uniform admixture of about 79 per cent nitrogen.

---

[a] Wien. Ber. Math. Nat. Kl. **61**, II, 367; **62**, II, 468.

[b] Wien. Ber. Math. Nat. Kl. **85**, II, 147 and 748; **7**, II, 188; **96**, II, 546.

The soils upon which the experiments were made were two slightly moist sands, one very uniform and the other containing both fine and very coarse grains; a clay loam in three states, air dry, with 19.6 per cent water, and with 20.1 per cent water; and a garden loam, air dry and with 18.6 per cent water. In view of these great variations in texture and structure, it seems safe to conclude that the result just obtained is a general one, and may be applied to all soils without danger of any very great errors.

Before pursuing this subject further, we shall return to the consideration of Table II, and see whether there is any obvious relation between the transpiration constant and the porosity.

RELATION BETWEEN POROSITY AND SPEED OF TRANSPIRATION.

By making an assumption similar to that made about the relation of porosity and diffusion, namely, by assuming that there is a relation of the form

$$T = \text{constant} \times D^{\beta}$$

we may compute the values of β; these values will be found in column VII of Table II. The eighth and twelfth values fall considerably below the others, and it thus appears probable that when, as in these two experiments, the decrease of porosity is caused by the addition of water, the variation of the transpiration with porosity is not the same as when the soil is compressed. In the case of the diffusion constant, these two experiments show no such peculiarities.

The values of β vary considerably; their mean, omitting the two values mentioned, is $\beta = 3.9 \pm 0.5$. The mean, omitting the value 10.32, which for other reasons appears doubtful, is $\beta = 3.17 \pm 0.18$.

If instead of computing β—i. e., trying to find a relation between transpiration and diffusion—we try to find a relation directly between porosity and transpiration, assuming the relation to be of the form

$$T = \text{constant} \times S^{\gamma}$$

we get, by making the same omissions as above $\gamma = 7.2 \pm 0.7$ and $\gamma = 6.47 \pm 0.45$. These relations, even if thoroughly established by more numerous and more accurate data, would be of no great importance; but it is interesting to note that changes in porosity due to consolidation of the soil by compression or tamping have an enormous influence on the freedom with which air flows through the soil under the influence of differences of pressure, the speed of transpiration varying as the sixth or seventh power of the pore space. If, for example, we roll a soil, and so decrease the porosity of the surface layer from 60 per cent to 40 per cent, or in the ratio of 3 to 2, we shall probably decrease the ease with which air flows in and out under the influence of barometric changes to as little as $(\frac{2}{3})^6$, or about 9 per cent of its former value.

We found that diffusion was nearly independent of structure and texture, but this is by no means true of transpiration. If we take the equation

$$T=K.S^{\gamma}$$

which, as we have seen, gives a rough idea of the relative variations of transpiration and porosity, and compute the values of the constant K from our experiments, using for each set of experiments the mean value of γ found for that set, we find that K varies as much as from 7 to 580, being lowest for the air-dry garden loam which contained a great deal of very fine material. The largest value was for the Cecil clay worked with 20.1 per cent of water. The other set of experiments on the same soil with nearly the same moisture content (19.6 per cent) gave a value of only about 60 instead of 580. The soil had been air dried and had become lumpy between the two experiments, and though the intention was to work it up in the second case (20.1 per cent) as nearly as possible like the first, it is evident enough from the difference in the ease of transpiration that this end was not attained. The diffusion constants show no such difference. It is obvious that in attempting to draw conclusions from experiments on transpiration great caution must be used, and that the porosity must be determined with much greater accuracy than has been done here in order to make numerical conclusions have any serious significance.

THE PENETRATION OF BAROMETRIC WAVES INTO THE SOIL.

We now know something of the ease with which air may be driven through certain soils by a difference of pressure. The actual values found for the transpiration constant varied from 84 down to 0.1, the latter value being for the air-dry garden loam, with a porosity of 43 per cent. In some of the experiments where soils had been wet up by opening the soil case and adding water from on top, the transpiration, under differences of pressure of from 5 mm. to 10 mm. of mercury, was too small to be measured, so that in nearly saturated soils the transpiration constant may become very much smaller than any of the values we have given. We want now to get an idea of how much air is actually driven into the soil by a rise in the barometric pressure, and how much comes out again when the pressure falls to its original value, so as to see how important this rinsing action may possibly be, and how deep it may extend. For this purpose we shall have to start with ideally simple conditions, and then compare the results with actual conditions, and in the course of our work we shall apply our computations to some actual meteorological data, so as to get an idea of what might be conceived to happen in reality under field conditions.

Suppose that over a certain region the barometer rises, i. e., the pressure of the atmosphere increases. If we assume that the barometer has been steady for some time, the air all through the soil down to the water table or impervious stratum will be at the same pressure as the outside air before the increase of pressure begins. If the soil be sufficiently open there is free communication of pressure between the soil air and the outside air, and as the outside pressure increases, that of the soil air must also increase by the same amount. Hence the air in the soil is compressed to a smaller volume and more air enters from outside. It is evident that if the outside pressure increases from 760 mm. to 761 mm. the air in the soil will be compressed to $\frac{760}{761}$ of its former volume, and, therefore, since the total free pore space in the soil is unchanged, that there must enter the soil from the outside a volume of air equal to one seven-hundred-and-sixty-first part of what was there already. For the present we shall speak as if this outside air were sharply divided from the soil air, though we shall see later that this is far from true. Looking at it in this way, however, we see that with an increase of pressure from 760 mm. to 761 mm. the outside air will advance into the soil to a depth which is $\frac{1}{761}$ of the total depth of the porous soil, supposed to have uniform porosity.

If, then, the soil be porous enough to permit this free communication of pressure, we may, by studying the barograph records for any given place, find the depths to which the outside air there has been advancing and from which it has been retreating during the period of the barograph records, in terms of the depth of the soil. If in addition we know the depth of the impervious layer we can compute these depths of penetration in inches or centimeters. The depth in each case will be the product of the depth of the soil by the fractional variation[a] of the barometric height. For example: If there is a variation of pressure of 0.1 inch, and the mean pressure is 30 inches, the pressure varies by $\frac{1}{300}$ of its value, or we may say that the fractional variation is $\frac{1}{300}$. If the soil were 40 feet deep, the depth of penetration would then be $\frac{1}{300} \times 40$ feet, or $\frac{2}{15}$ of a foot, i. e., 1.6 inches.

The volumes of air involved may be found by multiplying these depths by the area of soil surface under consideration.

We have stipulated that the pressure in the soil should be always and everywhere identical with the outside pressure, but this is only a limiting case which is never reached but is approached more and more nearly as the transpiration constant of the soil becomes larger and larger, or the barometric changes slower and slower. In reality the barometric changes have a finite speed and the soil offers some resistance to the passage of air through it; hence the pressure at any point in the soil will vary less than the outside pressure, and the amplitude of the variation will decrease as we go deeper down into the soil. Furthermore, there will be a certain amount of time lag, by which we mean that the variations of pressure at any point in the soil will not be simultaneous with the variations of the outside pressure, but will lag somewhat behind them. For these reasons the depths of penetration and amounts of rinsing which we might compute by the method just described are only limiting maximum values which are never quite reached.

---

[a] By "fractional variation" we mean the actual variation divided by the mean pressure of 760 mm. or the actual variation expressed as a fraction of the total value of the varying quantity.

To find the true values in any actual case is altogether impossible, because of the irregular manner in which the outside pressure changes; but it is, nevertheless, worth while to try to find out how far the actual values fall below these maxima for certain assumed values of the depth, porosity, and transpiration constant of the soil, and for a simple periodic oscillation of the outside pressure. Mathematically speaking, the problem is identical with a problem in heat conduction, and it may be treated by the same methods. An outline of the mathematical work will be given in Appendix A, and we shall state here only the results of the computations for a few cases.

As has been mentioned, the actual variations of the barometric pressure are so irregular as altogether to preclude the possibility of a strict mathematical treatment. We must, therefore, make some simplifying assumption regarding the changes of outside pressure. We shall assume that the pressure is oscillating regularly through a small constant range on each side of the mean value, and we shall assume that this state of affairs has already existed for a very long time, so that the effects of any previous state of affairs have vanished. The oscillations of pressure are to be of the simplest possible nature, what is known as a simple harmonic oscillation. The amplitude of the oscillation—i. e., the greatest departure of the outside pressure from the mean value—we shall denote by p_0. The actual divergence of the pressure at any point in the soil and at any time from its mean value will be denoted by p. What we do first is to find the average value of p from the surface down to the impervious stratum, i. e., how much at any instant the pressure in the soil all the way from the surface down to the impervious stratum differs on the average from the mean barometric pressure. As the outside pressure varies up and down, this average pressure in the soil will also vary up and down through a certain range which is smaller than the range or amplitude of the outside pressure. What we want to do finally is to find out how great this range is; i. e., we want to find the amplitude of the average pressure in the soil in terms of the amplitude of the outside pressure. We shall denote this amplitude by P. What we really want, then, is the value of $\frac{P}{p_0}$, or, in other words, the ratio of the maximum variation of the mean pressure in the soil to the maximum variation of the outside pressure.

It is evident that if the ease of transpiration be great enough the pressure in the soil will be everywhere and at all times sensibly the same as the outside pressure, or that the ratio $\frac{P}{p_0}$ will be sensibly equal to one. The ideal case of which we first spoke is thus characterized by the value $\frac{P}{p_0}=1$. If the depth of the soil be very great, or if the barometric oscillations be very rapid, it is obvious that the changes in pressure in the soils will be smaller than those outside, so that $\frac{P}{p_0}$ will be less than one, and may have any value whatever down to zero as its inferior limit.

We shall now give a few of the computed values of $\frac{P}{p_0}$ for various assumed values of the depth, porosity, and transpiration constant of the soil and for regular barometric oscillations of various periods. In any one case the transpiration constant and porosity are assumed to be constant, i. e., the soil is assumed to have the same physical properties, as regards transpiration, at least, all the way from the surface to the bottom of the soil atmosphere.

Case I.—Porosity = 30 per cent.
Transpiration constant = 1.00.
Depth to impervious stratum = 15 meters (49.3 feet).

(*a*) For a variation with a period of 1 day, $\frac{P}{p_0}=1.0$ sensibly.

(*b*) For a variation with a period of 1 hour, $\frac{P}{p_0}=0.86$.

For any smaller depth of soil, for a larger transpiration constant, or for slower waves of pressure, the value of $\frac{P}{p_0}$ will approach one more nearly. Even for a soil as deep as 49 feet and for waves as rapid as one an hour, the variations of the mean pressure in the soil are 86 per cent of the outside variations for a transpiration constant of one.

Case II.—If under the foregoing conditions the soil be only 5 meters deep (16.4 feet), $\frac{P}{p_0}$ will be sensibly equal to one for hourly waves, and for fifteen-minute waves its value will be 0.96.

Case III.—Porosity = 20 per cent.
Transpiration constant = 0.01. (The lowest value we measured was 0.1, so that this soil is ten times more impervious than the most impervious on which measurements were actually made.)
Depth to impervious stratum = 15 meters (49.3 feet).

For three-day waves. $\frac{P}{p_0}=0.87$. Even in this very deep, compact, and impervious soil the amplitude of the average soil pressure for a three-day wave is 87 per cent of the outside amplitude.

Case IV.—Porosity = 40 per cent.
Transpiration constant = 1.0.
Depth of soil = 1 meter (3.3 feet).

For waves with a period of 1 minute, $\frac{P}{p_0}=0.98$.

Barometric variations of a period shorter than half a day are in general of small amount, and the important cases among those cited are those for which the period of the waves is twelve hours or more; i. e., those of the semidiurnal, diurnal, and slower waves.

It may be seen from the figures just given that in general, for those variations of pressure which are slow enough to be of important magnitude, the value of $\frac{P}{p_0}$ does not, even for a soil nearly 50 feet deep, fall very much short of unity for such reasonable values of the transpiration constant as have been assumed. In other words, the mean pressure in the soil does follow the outside pressure fairly closely, so that the ideal case with which we started is not very far from representing the truth, at least for regular periodic variations of pressure. Soils may of course be found where the transpiration constant is much less than 0.01, and in these cases the lag and damping of the pressure waves as they run down into the soil will be greater and the values of $\frac{P}{p_0}$ less. We have gone through these computations because we had beforehand no idea of what to expect. If we had found for such reasonable cases as those just discussed that the value of $\frac{P}{p_0}$ was nearly zero, we should have known at once that our simple method of computing the depth of penetration of the outside air into the soil was altogether useless and could only give values far in excess of the truth. As it is, we have seen that in some cases which might very well occur in practice, daily or slower waves of pressure may, even in a deep soil, penetrate almost unretarded, so that if no other disturbing factor came in, our simple computation of the rinsing effect might correspond to reality. In any case the values we compute by this method are maximum values which may often be nearly reached, but in other cases not. Our computations will, at any rate, never give us too small values for the penetration and rinsing effect.

Let us, then, assume that the soil conditions are such as to permit free and instantaneous communication of pressure, so that the mean pressure in the soil is at all times the same as the barometric pressure outside, and let us see what depth of penetration we may expect in a actual cases.

VARIATIONS OF PRESSURE ACTUALLY TO BE EXPECTED.

For this purpose we must have some data regarding the barometric variations to be expected. By the courtesy of the officials of the Weather Bureau we were enabled to examine the barograph sheets for the summer of 1903 for Bismarck, N. Dak., Eastport, Me., and San Antonio, Tex. For the last two stations the examination extended from April 1 to September 30, while for Bismarck it stopped at August 31. To get an exact value for the diurnal or semidiurnal range would, of course, require a very careful analysis of the records for many years, but a rough and ready examination of the records for these three widely separated stations and for one growing season will give us a general idea of the order of magnitude of the variations in question. The method pursued was as follows:

The value of each pronounced maximum or minimum was recorded, and by subtraction were obtained the magnitudes of the successive changes from high to low, low to high, etc. It was found that in general there were a few large changes and a great many very much smaller ones. The value 0.20 inch was chosen arbitrarily as the dividing line, and the variations were divided into two classes; (1) those equal to or greater than 0.20 inch, and (2) those less than 0.20 inch. The smaller variations were classed as due to diurnal or semidiurnal waves of pressure. In the course of a large variation, several smaller ones, while their presence was indicated, might fail to give maxima or minima, and so not be counted. Hence the number of daily waves counted must be expected to come out smaller than the number of days. This was the case with the small waves for Bismarck and Eastport. For San Antonio the most marked oscillation appeared to be semidiurnal, the number of small oscillations counted being much more than the number of days, though less than twice that number. The results of the examination of these smaller waves may be tabulated as follows:

TABLE III.

Station.	Total number of variations.	Sum of the variations.	Number of days.	Sum ÷ number of half days.	Sum ÷ number of quarter days.	Mean amplitude in mm.	Period.	Mean fractional amplitude.[a]
		Inches.		*Inch.*	*Inch.*		*Day.*	
Bismarck	151	13.60	153	0.044	....	0.56	1	0.00074
Eastport	195	11.62	183	.032	....	.41	1	.00054
San Antonio	466	39.87	183	....	0.055	.69	.5	.00091

[a] By the "fractional amplitude" we mean the actual amplitude in inches divided by 30, or the ratio of the amplitude to the whole value of the pressure.

At Bismarck and Eastport there was, therefore, a mean daily oscillation of the pressure of from 0.0005 to 0.0008 of an atmosphere on each side of the mean, while at San Antonio there was a half-daily oscillation of about 0.0009, or somewhat more.

Along with these smaller waves go the larger ones, due to the passage of high and low pressure areas. At Eastport these came in a fairly regular succession. At Bismarck they were somewhat less regular and of about the same amplitude. At San Antonio they were much fewer, less regular, and of distinctly smaller amplitude. These larger waves may be tabulated as follows:

TABLE IV.

Station.	Number of waves.	Number of days.	Mean period.	Mean amplitude.	Mean fractional amplitude.
			Days.	*mm.*	
Bismarck	39	153	3.9	5.0	0.0066
Eastport	35	183	5.2	4.6	.0060
San Antonio	10	183	18.3	3.7	.0048

These long-period waves thus caused an oscillation of the pressure of from 0.004 to 0.007 of an atmosphere above and below its mean value. On the whole they have about ten times the amplitude of the smaller waves already considered.

ACTUAL AMOUNTS OF RINSING POSSIBLE.

It is now a very easy matter to see how far into the soil the rinsing action of these waves would extend if the division between soil air and outside air remained sharp. The distance of penetration is twice the fractional amplitude of the wave multiplied by the depth of the soil, always supposing that $\frac{P}{p_0}$ does not differ much from unity. Suppose that we take fractional amplitudes of about the magnitudes found for the short waves and for the long waves at the stations mentioned. The depths of penetration in inches are given below for various depths of soil, on the assumption that $\frac{P}{p_0}=1$.

TABLE V.

Fractional amplitude.	Depth of penetration where depth of soil is—			
	10 feet.	25 feet.	50 feet.	100 feet.
	Inches.	*Inches.*	*Inches.*	*Inches.*
0.0005	0.12	0.30	0.60	1.2
0.0007	.17	.42	.85	1.7
0.0009	.22	.54	1.10	2.2
0.005	1.2	3.0	6.0	12.0
0.007	1.7	4.2	8.5	17.0
0.009	2.2	5.4	11.0	22.0

These are maximum values which could not be exceeded. If $\frac{P}{p_0} < 1$ they would not be reached. It is highly improbable that for a soil as deep as 100 feet the transpiration would be free enough to make $\frac{P}{p_0}$ even approximately equal to 1, so that the values given in the last column are probably larger than would ever be reached in practice. This table gives us a fair idea of the depth to which the rinsing action would extend at the three places named for various depths of soil. It may be seen that the daily and half-daily waves would not penetrate more than an inch except for very deep soils. The longer and larger waves would cause a deeper rinsing, but it would not happen so often.

We have thus obtained an idea of the possible amount of rinsing action or aeration to which the soil might be subject at places where the variations of the barometer were somewhat similar to those which occurred at Bismarck, Eastport, and San Antonio during the summer of 1903, if the action were not complicated by diffusion. We must next turn our attention to diffusion and see how fast a soil would be aerated, i. e., how fast a gas such as carbonic acid would escape and be replaced by oxygen by diffusion alone if the barometer were steady. Afterwards we must see how the two causes of aeration work together to produce the actual result.

THE MOVEMENT OF GASES THROUGH SOILS BY PURE DIFFUSION.

THE FREE DIFFUSION OF TWO GASES.

If two gases are placed in contact they mix at a definite rate which depends upon the nature of the two gases, the temperature, the total pressure, and the linear rate of variation of the partial pressure of each gas. This speed of mixing by diffusion is usually characterized by the diffusion coefficient which is defined as follows:

The diffusion coefficient K is the number of cubic centimeters of each gas, measured at 760 mm. and at t°, the temperature of the experiment, which would at a temperature t° pass in one second through 1 cm^2 into the other gas, if the rate of change of the partial pressure of each gas in a direction perpendicular to the square centimeter were 760 mm. of mercury per centimeter. The theory of Stefan,[a] confirmed by the experiments of Loschmidt[b] and others, shows that this coefficient K is proportional to the square of the absolute temperature, inversely proportional to the total pressure, and inversely proportional to the square root of the product of the densities of the two gases. These relations do not appear to be absolutely exact, but the first two are fairly so. The values of K have been measured for various pairs of gases under definite conditions, and we have already, in discussing our experimental results, referred to the values obtained by Loschmidt and Obermayer for the diffusion of air and carbonic acid into each other. If this rate of diffusion be known for one set of conditions of temperature, total pressure, and partial-pressure gradient, it may be computed for any other set of conditions.

---

[a] Wien. Ber. Math.-Nat. Kl., 63, II, 63.

[b] Loc. cit.

The discussion just referred to showed that diffusion of air and carbonic acid through the soil was in fact merely a modified case of free diffusion, our results, when properly reduced, being entirely consistent with those obtained for diffusion when no soil was present. We are therefore justified in assuming that the laws of free diffusion are still applicable, even in a slightly less simple case than that on which our experiments were made, and we shall make use of these laws in the consideration of what must happen in a soil where we have, not a simple case of the mixing of carbonic acid and air, but a mixing of carbonic acid and oxygen which have to move by diffusion, not only through each other, but through a nearly uniform admixture of about 79 per cent nitrogen.

THE DIFFUSION OF TWO GASES THROUGH A THIRD GAS.

We have, therefore, to consider the case of the free diffusion of two gases through a third, which at the start is uniformly distributed, so that its partial pressure is everywhere the same.

The theory of Stefan,[a] confirmed by the experiments of Wretschko[b] and Benigar,[c] shows in the first place that the third or neutral gas, which at the start was uniformly distributed, will not remain so, but will be forced toward the place from which the lighter of the other two gases is coming so as to become slightly more concentrated there. In the second place, it shows that the rates of motion of the two other gases will no longer be equal, as when no third gas is present, and that both rates will be modified by the presence of the third gas. Furthermore, the theory shows how these rates may be computed from the rates for the three gases taken in separate pairs.

THE DISTRIBUTION OF NITROGEN IN THE SOIL.

As regards the first of these points, it is interesting to refer to a set of experiments by Ebermayer[d] in which soil air drawn from the depths of 70 cm. (27.6 inches) and 15 cm. (5.9 inches) in a garden soil under various crop conditions was analyzed for oxygen and carbonic acid, so that the nitrogen may be found by subtraction, assuming that such other gases as may have been present were insignificant in amount. The soil was rich in lime and humus. It was covered with beech, pine, moss, or sod, or was left bare. The beech and pine are referred to as "plants," and were presumably small, the experiments having taken place in a nursery. A great many analyses were made during the period from January, 1886, to February, 1887, inclusive, and the average results may be tabulated as follows:

---

[a] Loc. cit.

[b] Wien. Ber. Math.-Nat. Kl., **62**, II, 575.

[c] Ibid., **62**, I, 687.

[d] Forsch. auf. d. Geb. d. Agr. Physik., **13**, 15, 1890.

Table VI.

Crop and depth.	N_2	CO_2	O_2	ΔN_2	$\frac{1}{2}[\Delta CO_2+\Delta O_2]$	$-\frac{\Delta N_2}{\frac{1}{2}(\Delta CO_2+\Delta O_2)}$
Beech:						
70 centimeters....	78.96	1.19	19.85	....	....	....
15 centimeters....	78.91	.62	20.47	−0.05	−0.60	−0.08
Pine:						
70 centimeters....	76.93	9.39	13.68	....	....	....
15 centimeters....	79.10	1.13	19.77	+2.17	−7.68	+ .28
Moss:						
70 centimeters....	78.19	7.98	13.83	....	....	....
15 centimeters....	78.93	1.93	19.14	+ .74	−5.69	+ .13
Sod:						
70 centimeters....	78.25	4.13	17.62	....	....	....
15 centimeters....	79.28	.60	20.12	+1.03	−3.02	+ .34
Bare ground:						
70 centimeters....	77.37	7.02	15.61	....	....	....
15 centimeters....	78.88	1.19	19.93	+1.51	−5.08	+ .30

An examination of this table discloses the following facts:

(1) The concentration of the nitrogen does not vary much, being always between 76.9 per cent and 79.3 per cent.

(2) With the exception of the case of the beech plantation, where the variation is very small, the percentage of nitrogen was higher at 15 cm. depth than at 70 cm. This is what we should expect, according to Stefan's theory; for the lighter gas, oxygen, is coming from above and the heavier gas, carbonic acid, from below.

(3) This difference in the concentration of nitrogen is greatest where the partial pressure gradients of the carbonic acid and the oxygen are greatest—i. e., where the speed of the diffusion process is greatest. In fact, if we omit the experiments under the beech plants, we find that the difference of concentration of the nitrogen at 70 cm. and 15 cm. is roughly proportional to the mean gradient of the oxygen and carbonic acid. This is shown by the approximate equality of the numbers given in the last column of the table. It thus appears that in this case there was a displacement of nitrogen due to the diffusion of carbonic acid and oxygen into each other through the nitrogen, as predicted by Stefan's theory and as observed by Wretschko in his experiments on oxygen, carbonic acid, and hydrogen.

It is probable that the soil conditions where these experiments were made were particularly simple, and therefore favorable for a confirmation of the theory, and under less simple conditions such a confirmation could hardly be expected. The relations might be disturbed and complicated by various causes, the most obvious of which is the escape of carbonic acid downward without any corresponding inflow of oxygen from below. If, for example, there were a considerable flow of ground water coming from places where there was less carbonic acid present in the soil air, the carbonic acid would be absorbed and removed by the water. This would cause an inflow from above of air as a whole, and since this inflow would come to mix with soil air which had already lost some of its oxygen during the formation of carbonic acid which had then itself been removed by the ground water, the result would be a tendency to make the soil air richer in nitrogen than the outside air and give an increasing percentage as the depth increased. This action would be opposed to the one just discussed, and might in some cases even reverse the total effect. This would be most likely to happen in cases where the gradients of carbonic acid and oxygen were small and the diffusion weak.

With the exception of the experiments of Ebermayer already referred to, we have found only one other set of figures bearing on this point. They are quoted by Sachsse[a] from experiments by Fleck,[b] and, as far as they go, show just the opposite of Ebermayer's results. The experiments were on a garden soil, analysis being made of air drawn from the depths of 2, 4, and 6 meters. The average percentages of N_2, CO_2, and O_2 for the months April to November, inclusive, are shown in the following table:

TABLE VII.

Gas.	Depth.		
	2 meters.	4 meters.	6 meters.
	Per cent.	*Per cent.*	*Per cent.*
N_2	79.21	79.27	79.29
CO_2	2.82	4.26	5.47
O_2	17.97	16.47	15.24

The differences in the nitrogen are small, and in the results from which these averages were taken the oxygen is only given to 0.1 per cent, so that the difference of nitrogen at 2 meters and at 6 meters is of doubtful significance. However, such as the figures are they show an increase of nitrogen from the surface down to a depth of 6 meters, or 19.7 feet. It will be noticed that the gradients of carbonic acid and oxygen were very much smaller than in Ebermayer's experiments, so that the displacement upward, due to diffusion, would be much less.

---

[a] Lehrb. d. Agr. Chemie, pp. 144, 188.

[b] Jahresber. f. Agr. Chemie, 16 and 17 jahrg., p. 160.

even if no disturbing influences were present. In Ebermayer's experiments the mean gradient of carbonic acid was 0.108 per cent per centimeter. In Fleck's experiments it was 0.0066 per cent per centimeter, or only 0.06 of that in Ebermayer's experiments; hence we should expect only 0.06 of the effect. The greatest displacement of nitrogen shown by Ebermayer's experiments was 2.4 per cent in 55 cm., which at the same rate would amount to 17.5 per cent in 4 meters. With a gradient only 0.06 as great we should, therefore, expect a difference of 0.06×17.5, or 1.05 per cent, at most, if no disturbing causes had interfered and if the conditions had been the same as in that one of Ebermayer's experiments which gave the greatest effect. Now, the soil at a depth of from 2 to 6 meters doubtless had a much smaller porosity than from 15 to 70 cm., so that the diffusion, and hence the displacement, of nitrogen would undoubtedly be much slower for given gradients of partial pressure. Hence it is easily conceivable that the tendency of the diffusion to cause a displacement of the nitrogen upward may have been slightly more than counterbalanced by some such action as that of the flowing ground water to which we have referred.

We may thus say that of the only two sets of experiments we have found bearing on the question, one, and that the more extensive, agrees well with the predictions of theory, and the other is inconclusive. In the exceptional case of the beech plantation in Ebermayer's experiments there was also only a very slight gradient of carbonic acid and oxygen compared with the other sets, so that this may fall under the same category as Fleck's results.

THE RATES OF DIFFUSION OF CARBONIC ACID AND OXYGEN THROUGH NITROGEN.

Besides predicting a displacement of the nitrogen toward the oxygen side, Stefan's theory also enables us to compute, approximately at least, the diffusion coefficients of oxygen and carbonic acid in a mixture where we have 79 per cent of nitrogen and 21 per cent of carbonic acid and oxygen together. In this case the mean rate of diffusion is about 1.12 times the rate for the two gases without the nitrogen. If from the mean of Loschmidt's and Obermayer's measurements on free diffusion we now compute the mean diffusion constant for oxygen and carbonic acid diffusing through 79 per cent of nitrogen, we find the value:

$$D_f = 0.00073$$

where D_f is the mean number of cubic centimeters of each gas measured at 760 mm. and 25° C., which would in one second pass into the other through an admixture of 79 per cent nitrogen, through each square centimeter of cross section, if the concentration of each gas varied in a direction perpendicular to the square centimeter at the rate of 1 per cent per inch, if the total pressure were 760 mm. and if the temperature were 25° C. This tells us the rate of free diffusion.

We shall now assume that the same relation holds for this sort of diffusion as we found to hold for the mixing of air and carbonic acid through a soil. We shall, namely, assume that if D_f be the rate for perfectly free diffusion, and if D_s be the rate of diffusion through a soil of the porosity S; then

$$D_s = D_f S^2$$

Using this relation we get the following values of D_s for various porosities of the soil for a pressure of 760 mm. and for a temperature of 25° C.

TABLE VIII.

S	0.2	0.3	0.4	0.5	0.6	0.7
D_s	0.000029	0.000065	0.000116	0.000182	0.00026	0.00036

These values of D_s show the rates at which carbonic acid would move upward by diffusion and be replaced by oxygen in soils of the respective porosities given, at places where the partial pressure gradient was such as to give a change of concentration of 1 per cent per inch of depth, the pressure being 760 mm. and the temperature 25° C.

In the following table are shown these rates of escape of carbonic acid and entrance of oxygen to replace it for various porosities of the soil and for various rates of change of concentration with the depth, and under the aforesaid conditions of pressure and temperature. The values are given in cubic feet per day per square foot of soil surface.

TABLE IX.

Change of concentration, per cent per inch.	Porosity.					
	0.2	0.3	0.4	0.5	0.6	0.7
0.1	0.0082	0.019	0.033	0.052	0.074	0.10
0.2	.0165	.037	.066	.103	.15	.20
0.3	.025	.056	.099	.16	.22	.30
0.4	.033	.074	.132	.21	.30	.40
0.5	.041	.093	.17	.26	.37	.51
0.6	.050	.111	.20	.31	.45	.61
0.7	.058	.130	.23	.36	.52	.71
0.8	.066	.15	.26	.41	.59	.81
0.9	.074	.17	.30	.46	.67	.91
1.0	.082	.19	.33	.52	.74	1.01

In any specific case, if we know the porosity of the soil and the concentration of carbonic acid a short distance below the surface, we may at once find from Table IX the rate at which carbonic acid is escaping from the soil; or, in other words, the rate at which it is being produced in the soil under the place in question. For example:

In a clay loam soil in a corn field on Brightwood avenue, District of Columbia, Mr. J. O. Belz found by analysis of air drawn from a depth of 6 inches, 1.20 per cent of CO_2. The mean gradient of carbonic acid near the surface of the soil was therefore $(1.20 \div 6)$, or 0.2 per cent per inch. The soil was well cultivated, and though no measurement on this point was made it is safe to assume that the porosity was between 50 and 60 per cent; in other words, that the quantity S, by which we represent the porosity, had a value of from 0.5 to 0.6. Looking at Table IX, in the second line, which corresponds to a gradient of 0.2 per cent per inch, we find the figures 0.103 for $S=0.5$ and 0.15 for $S=0.6$. This means that at that time and place carbonic acid was coming out of the soil at a rate of from 0.10 to 0.15 cubic foot per day for each square foot, and therefore that below the depth of 6 inches carbonic acid must have been in the course of production at that rate. This computation is, of course, made on the assumption that the state of affairs was not changing rapidly, and that analyses on the preceding and following days would not have given amounts of carbonic acid very different from 1.2 per cent at 6 inches. If the porosity had been measured we could have given the rate of escape, and therefore of production, more closely instead of having merely to give the limits of 0.1 and 0.15 cubic foot per day per square foot.

In another case Mr. Belz found in air drawn from a depth of 6 inches in a flower bed in front of the building of the Bureau of Soils 0.65 per cent of CO_2. The mean gradient near the surface was therefore about 0.1 per cent per inch. Mr. Belz estimates the porosity of the soil here as about 43 per cent. It is safe to say that it was between 40 and 50 per cent. By looking in the first line of Table IX, which gives the values for a gradient of 0.1 per cent per inch, we find for $S = 0.4$ the figure 0.033, and for $S = 0.5$ we find 0.052. We may say, then, that in this case carbonic acid was escaping from the soil at the rate of about 0.04 cubic foot per day per square foot, and therefore that this was the rate of production of carbonic acid in the soil at this place below the depth of 6 inches. Other similar cases might be treated in the same way.

If we had data on the percentage of carbonic acid and the porosity of the soil at different depths we could go still further and say how fast carbonic acid was being produced below certain given levels, and could then by subtraction find, approximately at least, how fast it was being produced *between* certain levels, and thus get an idea of how the production of carbonic acid was localized at different depths.

The converse of the foregoing problem may also be solved by the same principles. Suppose, for example, that we know by some means or other that in a given soil of 50 per cent porosity near the surface carbonic acid is being produced at the rate of 0.4 cubic foot per day under each square foot below the 6-inch level. By looking in Table IX, in the column headed 0.5, we find that a rate of escape of 0.4 cubic foot per day corresponds to a gradient of 0.78 per cent per inch of depth. At a depth of 6 inches we might therefore expect to find that the concentration of the carbonic acid was about 0.78×6, or 4.5 per cent.

To take a more concrete example: Mr. Belz found for untreated lawn soil from Takoma Park, Md., that when the soil had been shut up in a tight bottle for twenty-four hours the oxygen present had been reduced from the normal amount of 21 per cent to 10.6 per cent. The carbonic acid shown by the analysis had not increased to 10.4 per cent, as might at first sight have been expected, but only to 7.2 per cent, the deficit being due doubtless, in part at least, to absorption of some of the CO_2 formed by the 10 per cent of water which was present in the soil. Let us assume, however, that if there had been a steady state of affairs the oxygen which had vanished would all have been converted into carbonic acid so as to give 10.4 per cent of CO_2 at the end of the twenty-four hours.

Let us assume that under field conditions we have carbonic acid being produced at this average rate in a soil down to the depth of 10 feet. Suppose the mean porosity of the soil to be 30 per cent. The total free pore space under 1 square foot of surface and from the depth of 6 inches down to the depth of 10 feet will, in this case, be 30 per cent of 9½ cubic feet, or 2.85 cubic feet. Suppose, then, that carbonic acid is produced at such a rate as would give 10.4 per cent of carbonic acid if this soil were shut up tight for one day. The actual volume of carbonic acid produced will evidently be 10.4 per cent of 2.85 cubic feet, or very nearly 0.30 cubic foot. This, then, 0.30 cubic foot per day, is the rate at which carbonic acid will be produced under each square foot of soil surface below the depth of 6 inches, and if the state is a steady one carbonic acid must be escaping from the soil at this rate.

Suppose now that the surface soil to a depth of 6 inches has a porosity of 50 per cent. Then by consulting Table IX we may find what must be the mean gradient of carbonic acid in the first 6 inches in order to allow this rate of escape. By looking in the column headed 0.5, i. e., giving the values for a porosity of 50 per cent, we find that a rate of escape of 0.30 cubic foot per day requires a gradient of 0.58 per cent per inch. Hence the concentration at the depth of 6 inches would be found to be 0.58×6, or about 3.5 per cent.

THE EFFECT OF BAROMETRIC CHANGES ON THE ESCAPE OF CARBONIC ACID BY DIFFUSION.

We have investigated the flow of air into and out from the soil by transpiration under the influence of changes in the barometric pressure, and we have compared our results with the barometric data for the summer of 1903 at three widely separated stations. We have investigated the escape of carbonic acid from the soil and the entrance of oxygen to replace it by diffusion, and we have shown how to apply the results numerically to any actual case on the assumption that our experimental results represented general facts. We have made these investigations separately, considering each process as it would go on if the other were absent. We have now to consider how the two processes are combined to give the actual aeration of the soil. A mathematical treatment would lead to differential equations too difficult for solution, but we may get an idea of what happens by more elementary and non-mathematical reasoning, which, in view of the rough approximation of our experimental data, will be quite sufficient for the purpose in hand.

We have already shown how far the outside air might be expected to penetrate the soil during changes of pressure, for soils of various depths and for such variations of pressure as occurred during the summer of 1903 at Bismarck, Eastport, and San Antonio, if the soil were open enough to permit free communication of pressure, and if the outside air really remained distinguished from the soil air by a reasonably sharp dividing surface. The velocities of the transpiration waves are so small that we need not consider any possible disturbance of the sharpness of division by convection currents, but we must turn our attention to a comparison of these transpiration velocities with the probable velocities of diffusion and see whether our fiction of a sharp dividing surface has any semblance of reality. Real sharpness of division could exist only if the linear velocities of diffusion were insignificant in comparison with the rates of advance and retreat of the outside air due to transpiration. Let us compute these velocities for some particular cases.

Let us consider a fairly compact surface soil with a porosity of 40 per cent, i. e., let $S=0.4$. By referring to Table IX, we find that for a concentration gradient of 0.1 per cent per inch the speed of escape of carbonic acid would be 0.033 cubic foot per square foot per day. As usual, the temperature is supposed to be 25° C., or 77° F., which is a reasonable figure for the soil temperature, though perhaps rather low. Let us see what the linear velocity of the gas will be in this case.

We have seen (Table V) that in general the barometric transpiration waves would, on the assumption of a sharp surface of division, penetrate only a few inches below the surface of the soil. Let us fix our attention on a depth of 6 inches. From a very large number of analyses of soil air from various soils and under various crops, the highest percentage of carbonic acid quoted by Ebermayer, at a depth of 15 cm., or 5.9 inches, was 4.6. The great majority of cases gave less than 1 per cent. Let us take 2 per cent as an average, which is certainly high enough. If the concentration of the carbonic acid is only 2 per cent, its linear velocity will be fifty times its rate of escape, measured in cubic feet per square foot per day. This gives us, in the case just mentioned, a linear velocity of 50×0.033, or 1.65 feet per day. This is the linear velocity of free diffusion at a point where the concentration is 2 per cent and the gradient 0.1 per cent per inch; it is proportional inversely to the concentration and will therefore be greater and greater near the surface as the concentration is less and less.

The concentration of 2 per cent at 6 inches depth gives a mean gradient from there to the surface of one-third per cent instead of 0.1 per cent per inch, so that the linear velocity will be greater than 1.65 in the ratio of $\frac{1}{3}$ to $\frac{1}{10}$. This gives us the value $1.65\times\frac{1}{3}\div\frac{1}{10}$; or, we may write for the linear velocity of diffusion in this case

$$V_D=5.5 \text{ feet per day.}$$

Let us compare this velocity with the linear velocities of advance of the barometric waves into the soil, supposing them to remain sharp. First, let us take the four-day wave at Bismarck. This had a fractional amplitude (see Table IV) of 0.0066. In a soil 50 feet deep this wave would penetrate to a depth of $2\times0.0066\times50$, or 0.66 foot once in four days. The mean rate of motion of its surface would therefore be 0.66 foot in two days, or 0.33 foot per day, and we may write for this case

$$V_T=0.33 \text{ foot per day.}$$

We have, therefore,

$$\frac{V_D}{V_T}=\frac{5.5}{0.33}=17,$$

or, in other words, the mean linear velocity of transpiration is one-seventeenth of the velocity of diffusion in the case treated. The five-day wave at Eastport would give a somewhat smaller value of V_T, which would therefore be a smaller fraction of V_D.

Let us next consider the largest of the smaller barometric waves found, the half-daily wave at San Antonio. This had a fractional amplitude of 0.00091 (see Table III), and in a soil 50 feet deep would in the ideal case penetrate to a depth of $2\times0.00091\times50$, or 0.091 foot. Its mean linear velocity would therefore be 0.091 foot in one-quarter of a day, or 0.36 foot per day, so that we have for this wave

$$V_T=0.36 \text{ foot per day}$$

and

$$\frac{V_D}{V_T}=15,$$

or, in other words, the mean linear velocity of this wave is one-fifteenth of the velocity of diffusion in the case we are comparing it with. The daily waves at Bismarck and Eastport would give linear velocities of about seven-eighteenths and five-eighteenths of this, or only about one-third, thus giving values of $\frac{V_D}{V_T}$ about three times as large as those found above.

In making these comparisons we have taken care to choose the conditions favorably for the velocity of the transpiration wave in the following respects:

(1) We have assumed that there was perfectly free communication of pressure through the soil air, i. e., that $\frac{P}{P_0}=1$. This is a limiting maximum which will never be reached absolutely, and of which it may sometimes fall far short. In other words, we have computed the largest conceivable penetrations and hence the largest velocities of the barometric waves for a soil of the given depth.

(2) We have assumed that the soil was 50 feet deep to the water table or other impervious stratum. This is a large value. A smaller value would reduce our computed transpiration velocities in the same ratio.

(3) In computing the linear velocities of diffusion we have assumed a porosity of 40 per cent. This is a low value for the first few inches of a cultivated soil, and any larger value would increase the computed velocities of diffusion in proportion to the square of the porosity.

(4) We have considered the linear velocity of diffusion at a depth of 6 inches. This velocity increases greatly toward the surface as the concentration of the carbonic acid falls off toward the insignificant value of 0.03 per cent, which it has on the average in the outside air.

Thus we have made the conditions such as to give values above the truth for transpiration and below the truth for diffusion, and yet we have found that at most the linear transpiration velocity was only one-fifteenth of the linear diffusion velocity. In some cases, of course, the changes in the barometric pressure will be much larger and more sudden than those we have found, thus giving larger velocities of transpiration, but it is believed that the mean values which we have taken for a whole growing season and for three widely separated stations give a fair idea of what may be expected on the average.

As regards the assumption of 2 per cent carbonic acid at a depth of 6 inches, which was made arbitrarily for comparison, the following remarks may be made: If the concentration at that depth were only half as great, as it might very well be, the mean gradient up to the surface would be only half as great, and the rate of escape of the carbonic acid only half as great when measured in cubic feet per square foot per day, but the concentration being only half as great, the linear velocity for a given gradient would be twice as great. Hence, on the whole, though the *volume* escaping depends upon the gradient, i. e., on the rate of increase of concentration downward, the *linear velocity*, which is what we are here concerned with, is in fact independent of it, so that the arbitrariness of our selection of a case for comparison was perfectly legitimate and had no effect on the result, which would have been the same if we had assumed any other concentration at the depth of 6 inches.

There is, however, one more thing which, if allowed for, would increase the computed linear velocity of diffusion very considerably. We made the computations as if we had no soil present, or as if the given number of cubic feet which escape from 1 square foot of soil surface in a day had actually the whole cross section of 1 square foot through which to move. As a matter of fact the escape is taking place through only a part of this square foot, and the linear velocity must therefore be larger than computed just in proportion as the mean cross section of the free pore space in 1 square foot is less than the whole square foot. We have no means of knowing definitely what this ratio is, but the facts that we found the rate of diffusion to be proportional to the square of the porosity, and that free diffusion takes place proportionally to the sectional area of the tube along which it is taking place if the cross section only is varied, might very naturally lead us to assume that the mean effective cross section was proportional to the square of the porosity, in which case a soil with a porosity of 50 per cent would have only one-fourth of its cross section effective and so give four times the linear velocity of diffusion which we should get by computations such as are given above. But even though this form of reasoning may not be convincing, it is at any rate evident enough that the diffusion through 1 square foot is actually confined to channels of much less than 1 square foot in total cross section, so that the linear velocities which we have computed for diffusion should certainly be increased very considerably, though we can not say just how much.

The upshot of it all is, then, that in any average case the mean velocity of advance and retreat of the outside air through the soil surface under the influence of changing barometric pressure might perhaps be as high as one-twentieth of the linear velocity of diffusion, but is much more likely to be a great deal less. This means that the velocity of transpiration is altogether insignificant in comparison with the linear velocity of diffusion, and can therefore not have any important effect in modifying the rate of escape of carbonic acid from the soil and the entrance of oxygen to replace it. *This interchange goes on by diffusion, sensibly uninfluenced by the variations of the outside pressure.*

The velocity of diffusion, then, instead of being small, is very large in comparison with the velocity of advance and retreat of the barometric transpiration waves. Hence our ideal case of the inflow and outflow of the outside air with a sharp dividing surface between outside and soil air is a pure fiction. It does not correspond to the truth at all, and the rinsing which in the ideal case would be perfect once in each barometric oscillation down to the extreme depth of penetration of the wave is altogether insignificant, though, of course, something of the sort does exist.

If the front surface of the wave were sharp, there would be a slight increase of the rate of diffusion from lower layers, for in that case the free-air surface to which diffusion was taking place would be, on the average, not at the surface of the soil, but a little below it, thus decreasing the distance the carbonic acid had to transverse to escape, or giving a steeper gradient. But this action, like the rinsing effect on the surface layer, is seen to be insignificant when we consider the relative values, already discussed, of the linear velocities of diffusion and transpiration under such conditions as actually occur.

THE DIFFUSION OF OTHER GASES THROUGH THE SOIL.

Other gases than carbonic acid, nitrogen, and oxygen may be present in the soil or produced there. Their entrance or escape will follow the same laws as hold for carbonic acid and oxygen, and what would happen in any given case might be computed, if the necessary data were available, by the aid of the principles we have given. With the exception of water vapor, such gases are not, under normal conditions, present in large amounts, and are not known to be of any great importance to plant life, from an agricultural point of view, in comparison with the gases already mentioned. The original suggestion for the present research came from a desire to learn more about the diffusion of gases through soils because of its bearing on the escape of water from below the surface of a soil by other means than capillary motion of liquid water, and it is hoped to use the knowledge which has been gained here as a guide for further investigations on the drying out of soils.

CONCLUDING REMARKS.

In the course of the work described in the foregoing pages, we have done the following things:

(1) We have measured the rate of flow of air under pressure by transpiration, and of air and carbonic acid by diffusion, through four widely different soils, in varying states of structure, compactness, and moisture content.

(2) We have shown that the speed of diffusion of air and carbonic acid through these soils was not greatly dependent upon texture and structure, but was determined in the main by the porosity of the soil.

(3) We have shown that the rate of diffusion was approximately proportional to the square of the porosity.

(4) We have shown that when this relation is used to compute from our results the rate of free diffusion when no soil is present, it gives a result which is entirely consistent with what is already known from the work of other experimenters on the free diffusion of gases.

(5) We have shown that when the porosity of a soil is reduced by compacting it, the ease with which air flows through it under the driving influence of a difference of pressure is greatly reduced, varying as the sixth or seventh power of the porosity.

(6) We have investigated the depth to which free outside air might penetrate soils of different depths, under such barometric variations as are to be expected in average cases, if the outside air remained distinct from the soil air.

(7) We have shown how to compute the rate of escape of carbonic acid from the soil by diffusion under given conditions of temperature, pressure, porosity, and concentration of carbonic acid.

(8) We have compared the linear velocities of diffusion and barometric transpiration, and hence—

(9) We have shown that the escape of carbonic acid from the soil and its replacement by oxygen take place by diffusion and are determined by the conditions which affect diffusion, and are sensibly independent of the variations of the outside barometric pressure.

APPENDIX A.

THE PENETRATION OF BAROMETRIC WAVES INTO THE SOIL.

Let us assume, as the result of experiment, that when air moves through the soil under the driving influence of a gradient of pressure, the flow of air measured in cubic centimeters at 760 mm. is proportional to the pressure gradient. Consider a volume element $\delta x\ \delta y\ \delta z$, the flow being parallel to the axis of x, which we shall suppose measured vertically downward from the surface of the soil. The flow downward at x—i. e., into the element through its upper face—will be, in the time δt,

$$-T\ \delta y\ \delta z\ \frac{\partial p}{\partial x}\ \delta t,$$

if δx, δy, and δz are measured in centimeters, p in millimeters of mercury and t in seconds. In other words, if we take 1 square centimeter of soil 1 cm. thick and let the pressure vary by 1 mm. of mercury from one face to the other, the flow is T, and we may with these units use the values of T already tabulated. During the same time the flow of air downward at $x+\delta x$—i. e., out of the element through its lower face—is

$$-T\ \delta y\ \ \delta z\ \left[\frac{\partial p}{\partial x}+\frac{\partial}{\partial x}\left(\frac{\partial p}{\partial x}\right)\delta x\ \right]\delta t.$$

The total inflow is the first of these minus the second, or

$$T\ \delta x\ \delta y\ \delta z\ \frac{\partial^2 p}{\partial x^2}\ \delta t,$$

where we have assumed T to be a constant and independent of x and t.

If we let δQ be the amount of air flowing in, and replace $\delta x\ \delta y\ \delta z$ by δv, we have

$$\frac{\partial Q}{\partial t}=\quad\frac{\partial^2 p}{\partial x^2}\ \delta v. \tag{1}$$

If we let ρ be the cubic centimeters of gas measured at 760 mm. which are actually present per cubic centimeter of the soil, we have

$$\frac{1}{\delta v}\cdot\ \frac{\partial Q}{\partial t}=\frac{\partial \rho}{\partial t},$$

whence equation (1) takes the form

$$\frac{\partial \rho}{\partial t}=T\ \frac{\partial^2 p}{\partial x^2}. \tag{2}$$

If S is the pore space in 1 cubic centimeter of soil, we must evidently have

$$\frac{\rho}{S}=\frac{p}{760},$$

whence from (2) we get

$$\frac{\partial p}{\partial t}=\left(\frac{760\ T}{S}\right)\frac{\partial^2 p}{\partial x^2}, \tag{3}$$

or if we represent the essentially positive constant $\frac{760\,T}{S}$ by a^2, we have

$$\frac{\partial p}{\partial t}=a^2\frac{\partial^2 p}{\partial x^2}. \tag{4}$$

Now we are to consider small oscillations of pressure about a mean value of 760. Let us write

$$p=760+\theta,$$

where θ is the divergence of the actual pressure from its normal value of 760. We then have

$$\frac{\partial p}{\partial t}=\frac{\partial \theta}{\partial t};\quad \frac{\partial^2 p}{\partial x^2}=\frac{\partial^2 \theta}{\partial x^2};$$

or by substituting in equation (4),

$$\frac{\partial \theta}{\partial t}=a^2\frac{\partial^2 \theta}{\partial x^2}. \tag{5}$$

We have to find a solution of equation (5) which shall satisfy the initial and boundary conditions.

The initial condition is that at the start the excess of pressure θ shall be distributed in some determinate way as we go down from the surface to the bottom of the soil air at the impervious stratum, which we shall suppose to be at a depth $\frac{C}{2}$ cm. This condition, then, may be written

$$\theta=f(x),\text{ for } t=0.$$

We are going to consider the state of affairs after so long a time that the effect of the initial state shall have become negligible, so that the form of $f(x)$ is immaterial. We may, therefore, for simplicity write $f(x)=0$, and our condition becomes

$$\theta=0,\text{ for } t=0 \text{ and any value of } x \text{ from } 0 \text{ to } \frac{C}{2}.$$

Of the boundary conditions, one relates to the surface where the outside pressure varies periodically, and the other to the impervious layer at a depth $x=\frac{C}{2}$, through which no flow of air is possible. We shall assume that the outside pressure performs a simply harmonic oscillation of amplitude θ_0, and may therefore write our surface condition in the form

$$\theta=\theta_0 \sin \omega t,\text{ for } x=0 \text{ and any value of } t.$$

The maximum difference between the outside pressure and its mean value of 760 is θ_0. The period of the oscillation is $\tau=\frac{2\pi}{\omega}$.

The condition that for $x=\frac{C}{2}$ there shall be no flow of air in either direction is most easily satisfied by modifying the problem a little. Instead of imagining the soil air to stop at a depth $\frac{C}{2}$, let it continue to $x=C$, and at $x=C$ let there be a forced oscillation of pressure identical with that for $x=0$. The whole state of affairs will then be symmetrical about the point $x=\frac{C}{2}$, and there will be no flow through the surface at $x=\frac{C}{2}$, so that it is immaterial whether there is an impervious stratum at that depth or not, and a solution of our modified problem will be a solution of the original one. Our boundary conditions may, therefore, be satisfied by letting $\theta=\theta_0 \sin \omega t$, both for

$x=0$ and for $x=C$, so that we may now write all our conditions, initial and boundary, in the forms

$$(6)\qquad \begin{cases} \theta=0 & \text{for } t=0 \\ \theta=\theta_0 \sin \omega t & \text{for } x=0 \\ \theta=\theta_0 \sin \omega t & \text{for } x=c \end{cases}$$

The equation (5) must now be solved subject to the conditions (6). The solution may be found in Riemann's Partielle Differentialgleichungen (3rd ed., 1882, §§ 59, 60). It is

$$(7)\qquad \frac{\theta}{\theta_0}=\sin \omega t\left\{1-\frac{4}{\pi}\sum_{n=1,3,5}^{\infty}\frac{1}{n}\sin\frac{n\pi x}{c}\right\} +\frac{4a^2\pi}{c^2}\sum_{n=1,3,5}^{\infty} W n \sin\frac{n\pi x}{c}$$

where

$$(8)\qquad W=\int_0^t e^{-\left(\frac{an\pi}{c}\right)^2(t-\lambda)}\sin \omega\lambda d\lambda$$

If $t=\infty$ the value of W is found to be

$$(9)\qquad W=\frac{1}{\left(\frac{an\pi}{c}\right)^4+\omega^2}\left[\left(\frac{an\pi}{c}\right)^2\sin \omega t-\omega \cos \omega t\right]$$

which is the value we have to use, since we are concerned only with the state of affairs after a very long time, i. e., for very large values of t.

To simplify the work we now choose our unit of length equal to C, so as to make $C=1$ all through the equations. This changes the value of a^2 in a definite way. The value of a^2 is

$$a^2=\frac{760\ T}{S},$$

so that since S is a pure number, the dimensions of a^2 are the same as those of T. From the expression given on page 47 for the inflow of air into the left face of an element of volume, we have the dimensional equation

$$[l^3]=[Tl^2pl^{-1}t]$$

whence

$$[T]=[l^2p^{-1}t^{-1}] \quad ,$$

or since we are going to change only the unit of length we have for present purposes

$$[a^2]=[T]=[l^2] \quad .$$

This means that if, for instance, we increase the unit of length 10 times the value of a^2 will be decreased 100 times. Hence if we are treating a case where the depth to the water table is $\frac{C}{2}$ centimeters, we shall have to use in computing the value of a^2, not the value of T as measured in experimental units, but a value $\frac{1}{C^2}$ of that. Hence we must write, instead of $a^2=\frac{760\,T}{S}$.

$$(10)\qquad a^2=\frac{760T}{C^2S} \quad .$$

If we do this in our practical application to computing numerical results, we may write equations (7) and (9) in the forms

$$(11)\qquad \frac{\theta}{\theta_0}=\sin \omega t\left\{1-\frac{4}{\pi}\sum_{n=1,3,5}^{\infty}\frac{\sin n\pi x}{n}\right\}+4a^2\pi\sum_{n=1,3,5}^{\infty}Wn \sin n\pi x$$

$$W=\frac{1}{(an\pi)^4+\omega^2}\left[(an\pi)^2\sin\omega t-\omega\cos\omega t\right]\tag{12}$$

To find the average value of the pressure in the soil at any time we have to take $\int_0^1\frac{\theta}{\theta_0}\,dx$. If we let this mean value of θ be denoted by $\bar{\theta}$ and perform the integration, we get

$$\frac{1}{8a^2}\frac{\bar{\theta}}{\theta_0}=-A\ \omega\cos\omega t+B\ a^2\pi^2\sin\omega t\tag{13}$$

where

$$\begin{cases} A=\displaystyle\sum_{n=1,3,5}^{\infty}\frac{1}{(an\pi)^4+\omega^2} \\ B=\displaystyle\sum_{n=1,3,5}^{\infty}\frac{n^2}{(an\pi)^4+\omega^2} \end{cases}\tag{14}$$

The value of $\bar{\theta}$, or the deviation of the average pressure in the soil at any instant from its mean value of 760 mm. is evidently a periodic function of the time with the same period as the outside pressure. It must have a smaller amplitude and a certain time lag. The important thing for us is the amplitude, which we shall call $\bar{\theta}_o$. We want to find what is the greatest divergence of the mean pressure in the soil from the surface down to the water table from the normal pressure, or, in other words, we want the value of $\frac{\bar{\theta}_o}{\theta_o}$. To find this we must find the time for which $\frac{\bar{\theta}}{\theta_o}$ is a maximum or a minimum, and then insert this time in the general equation for $\frac{\bar{\theta}}{\theta_o}$, which will give us $\frac{\bar{\theta}_o}{\theta_o}$. By performing the usual operations of differentiation, etc., on equation (13) we get as our final result

$$\frac{1}{8a^2}\frac{\bar{\theta}_o}{\theta_o}=A\omega\cos\omega t+Ba^2\pi^2\sin\omega t,\tag{15}$$

where

$$A=\sum_{n=1,3,5}^{\infty}\frac{1}{(an\pi)^4+\omega^2}\tag{16}$$

$$B=\sum_{n=1,3,5}^{\infty}\frac{n^2}{(an\pi)^4+\omega^2}\tag{17}$$

and where t satisfies the condition

$$\tan\omega t=\frac{a^2\pi^2B}{\omega A}\tag{18}$$

In investigating any numerical case the first step, after deciding upon the porosity of the soil S, its transpiration constant T, and its depth $\frac{C}{2}$, as well as the period of the barometric oscillation, $\tau=\frac{2\pi}{\omega}$ (hourly, daily, etc.), was to use the numerical values decided upon to find the value of ω, and from equation (10) the value of a^2.

The next step was to compute approximate values of A and B [equations (16) and (17)]. Since the convergence of these series is inconveniently slow, two others were substituted. We have

$$\sum\frac{1}{(an\pi)^4+\omega^2}=\sum\frac{1}{(an\pi)^4}-\sum\left[\frac{1}{(an\pi)^4}-\frac{1}{(an\pi)^4+\omega^2}\right]$$
$$=\frac{1}{(a\pi)^4}\sum\frac{1}{n^4}-\sum\left[\frac{1}{(an\pi)^4}-\frac{1}{(an\pi)^4+\omega^2}\right]$$

The value of $\sum\limits_{n=1,3,5}^{\infty}\frac{1}{n^4}$ is $\frac{\pi^4}{96}$ and the auxiliary series $\sum\limits_{n=1,3,5}^{\infty}\left[\frac{1}{(an\pi)^4}-\frac{1}{(an\pi)^4+\omega^2}\right]$ converges fairly rapidly for most of the numerical cases treated. The value of B was found by a similar device, the known value on which the computation was based being in this case $\sum\limits_{n=1,3,5}^{\infty}\frac{1}{n^2}=\frac{\pi^2}{8}$.

After values had thus been found for A and B, they were inserted in equation (18). This gave the required values of sin ωt and cos ωt, which were finally substituted in equation (15), giving the desired value of $\frac{\bar{\theta}_o}{\theta_o}$, which then stated how far the oscillation of the mean pressure in the soil fell short, in its range, of the range of the oscillation of the outside barometric pressure, or, in other words, the error that would be committed by regarding the soil as so porous as to permit an absolutely free communication of pressure all through its volume from the surface down to the water table. The value of tan ωt found from equation (18) also permitted the computation of the time lag, but this is of no importance, as all we care about is the amount of pressure variation and not the time at which the maxima and minima of pressure occurred.

APPENDIX B.

THE DIFFUSION OF TWO GASES THROUGH A THIRD.

Stefan's theory of the diffusion of gases starts by forming the equations of motion of the gas in a volume element, considering the driving force to be the slope of pressure and assuming a frictional (or rather viscous) resistance to the motion of one gas through another which is proportional to the relative velocity of the two gases and to the product of their concentrations. The accelerations are then set equal to zero, as the motion is supposed to be so slow that kinetic energy is negligible. From this basis he deduces, for a pair of gases diffusing into each other, the equations

$$\frac{\partial p_1}{\partial t}=K\frac{\partial^2 p_2}{\partial x^2} \tag{1}$$

$$\frac{\partial p_2}{\partial t}=K\frac{\partial^2 p_2}{\partial x^2} \tag{2}$$

which had already been deduced by other methods. The diffusion constant K has the value

$$K=\frac{1}{b_{12}p} \tag{3}$$

where p is the total pressure and b_{12} a quantity which for a given temperature and a given pair of gases is constant. From a priori considerations, as well as from the results of experiment, it appears probable that b_{12} is proportional to the square root of the product of the molecular weights of the two gases.

He then extends his work to three gases, and shows that if the third gas remains sensibly uniformly distributed the other two have their velocities changed in known ways, so that we have

$$\frac{\partial p_1}{\partial t} = K' \frac{\partial^2 p_1}{\partial x^2} \tag{4}$$

$$\frac{\partial p_2}{\partial t} = K'' \frac{\partial^2 p_2}{\partial x^2} \tag{5}$$

where

$$K' = \frac{1}{b_{12}p - (b_{12} - b_{13})p_3} \tag{6}$$

$$K'' = \frac{1}{b_{12}p - (b_{12} - b_{23})p_3} \tag{7}$$

p_3 being the partial pressure of the third gas. The constants b_{13} and b_{23} have a similar significance to b_{12} which is to be found from the equation

$$K = \frac{1}{b_{12}p} \tag{8}$$

In our computation of the value of the diffusion constant of CO_2 and O_2 through an admixture of 79 per cent N_2, we used the relations $b_{12} / b_{13} / b_{23} = \sqrt{d_1 d_2} / \sqrt{d_1 d_3} / \sqrt{d_2 d_3}$ letting $d_1 / d_2 / d_3 = 44 / 32 / 28$, these being the relative densities of CO_2, O_2, and N_2. We also let $p_3 = 0.79\, p$, and took the necessary value of K from the mean result of Loschmidt and Obermayer, using the fact that K is proportional to θ^2 [where θ = absolute temperature, (273+25) in our case] to get the value of K at 25°. We were thus able to compute the diffusion constants K' and K''.

The values were

$$K' = 1.053\, K \text{ (for } CO_2)$$
$$K'' = 1.190\, K \text{ (for } O_2)$$

We took the mean of these, or 1.12 K, as the value to be used.

O